

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B32B 9/00, 15/04, B05D 3/00, 3/12, B28B 17/00, F03B 3/12, 7/00	A1	(11) International Publication Number: WO 97/01436 (43) International Publication Date: 16 January 1997 (16.01.97)
(21) International Application Number: PCT/US96/04461 (22) International Filing Date: 1 April 1996 (01.04.96) (30) Priority Data: 08/494,428 26 June 1995 (26.06.95) US (71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventors: HASZ, Wayne, Charles; R.D. #1, Box 376, Pownal, VT 05261 (US). BOROM, Marcus, Preston; Apartment B37, 1197 Hillside Avenue, Niskayuna, NY 12309 (US). JOHNSON, Curtis, Alan; 379 Vly Road, Schenectady, NY 12309 (US). (74) Agents: STECKLER, Henry, I. et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).		(81) Designated States: CH, DE, JP, KR. Published <i>With international search report.</i>
(54) Title: PROTECTED THERMAL BARRIER COATING COMPOSITE WITH MULTIPLE COATINGS (57) Abstract A composite that protects thermal barrier coatings from the deleterious effects of environmental contaminants at operational temperatures is discovered. The thermal barrier coated parts have at least two outer protective coatings that decrease infiltration of molten contaminant eutectic mixtures into openings in the thermal barrier coating.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

- 1 -

PROTECTED THERMAL BARRIER COATING
COMPOSITE WITH MULTIPLE COATINGS

FIELD OF THE INVENTION

The present invention relates to a composite that protects thermal barrier coatings deposited on gas turbine and other heat engine parts from the deleterious effects of environmental contaminants. Particularly, the invention relates to a composite thermal barrier coated part having multiple surface protective coatings on the ceramic thermal barrier coating.

BACKGROUND OF THE INVENTION

Thermal barrier coatings (TBCs) are deposited onto gas turbine and other heat engine parts to reduce heat flow and to limit the operating temperature of metal parts. These coatings generally are a ceramic material, such as chemically stabilized zirconia. Yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, and magnesia-stabilized zirconia are contemplated as thermal barrier coatings. The thermal barrier coating of choice is a yttria-stabilized zirconia ceramic coating. A typical thermal barrier coating comprises about 8 weight percent yttria-92 weight percent zirconia. The thickness of a thermal barrier coating depends on the application, but generally ranges between about 5-60 mils thick for high temperature engine parts.

Metal parts provided with thermal barrier coatings can be made from nickel, cobalt, and iron based superalloys. Thermal barrier coatings are especially suited for parts and hardware used in

- 2 -

turbines. Examples of turbine parts would be turbine blades, buckets, nozzles, combustion chamber liners, and the like.

Thermal barrier coatings are a key element
5 in current and future gas turbine engine designs expected to operate at high temperatures which produce high thermal barrier coating surface temperatures. The ideal system for a high temperature engine part consists of a strain-tolerant thermal barrier ceramic
10 layer deposited onto a bond coat which exhibits good corrosion resistance and closely matched thermal expansion coefficients.

Under service conditions, thermal barrier coated engine parts can be susceptible to various
15 modes of damage, including erosion, oxidation, and attack from environmental contaminants. At temperatures of engine operation adherence of these environmental contaminants on the hot thermal barrier coated surface can cause damage to the thermal barrier
20 coating. Environmental contaminants form compositions, which are liquid at the surface temperatures of thermal barrier coatings. Chemical and mechanical interactions occur between the environmental contaminant compositions and the thermal
25 barrier coatings. Molten contaminant compositions can dissolve the thermal barrier coating or can infiltrate its pores and openings, initiating and propagating cracks causing delamination and loss of thermal barrier coating material.

30 Some environmental contaminant compositions that deposit on thermal barrier coated surfaces contain oxides of calcium, magnesium, aluminum, silicon, and mixtures thereof. These oxides combine to form contaminant compositions comprising calcium-

SUBSTITUTE SHEET (RULE 26)

- 3 -

magnesium-aluminum-silicon-oxide systems (Ca-Mg-Al-Si-O), herein referred to as CMAS. Damage to thermal barrier coatings occurs when the molten CMAS infiltrates the thermal barrier coating. After infiltration and upon cooling, the molten CMAS, or other molten contaminant composition, solidifies. The stress build up in the thermal barrier coating is sufficient to cause spallation of the coating material and loss of the thermal protection that it provides to the underlying part.

There is a need to reduce or prevent the damage to thermal barrier coatings caused by the reaction or infiltration of molten contaminant compositions at the operating temperature of the engine. This can be accomplished by providing the TBC ceramic coat with multiple protective coatings that reduces damage to the thermal barrier coating from molten contaminants.

SUMMARY OF THE INVENTION

The present invention satisfies this need by providing a protected thermal barrier coating composite comprising at least two continuous protective coatings covering an outer surface of a thermal barrier coating. The invention also includes a protected thermal barrier coated engine part comprising an engine structural component with a bond coat, a thermal barrier coating on the bond coat and at least two protective layers on the thermal barrier coating. The protective coatings reduce or prevent attack of the thermal barrier coating from environmental contaminants and their corresponding contaminant compositions. Contemplated protective coatings include impermeable barrier coatings, sacrificial oxide coatings, and non-wetting coatings.

- 4 -

The invention includes a method for making a thermal barrier coating-protecting-composite which comprises depositing an impermeable barrier or sacrificial oxide first coating on the thermal barrier coating, and then depositing at least one other coating that is non-wetting, sacrificial or impermeable on the first coating.

Herein, the terms "impermeable barrier coating", "sacrificial oxide coating", and "non-wetting coating" are defined as follows.

An impermeable coating is defined as a protective layer which inhibits liquid contaminant compositions from infiltrating into or reacting with the thermal barrier coating at the operating temperature of the thermal barrier coating. The impermeable barrier is a dense, non-cracked, non-porous layer comprising oxides, non-oxides, or metallic coatings in conjunction with thermal barrier coatings.

A sacrificial oxide coating is defined as a layer which when in contact with the environmental contaminant composition raises the melting temperature or viscosity of the contaminant composition as it forms on the hot surfaces of the composite. As a result, the contaminant composition does not flow or form a reactive liquid. The sacrificial oxide coating undergoes chemical or physical changes when in contact with the contaminant composition at operating temperatures by dissolving in the contaminant composition or reacting with it to form a by-product material which is not liquid or at least more viscous than the original contaminant composition.

A non-wetting coating is defined as an outer layer which minimizes contact between underlying

SUBSTITUTE SHEET (RULE 26)

- 5 -

layers and the molten contaminant composition by providing a surface that is non-wetting to environmental contaminant compositions. As a result, the contaminant composition's ability to penetrate the thermal barrier coating via capillary action is decreased and the integrity of the composite at high temperature performance is enhanced.

Environmental contaminants are materials that exist in the environment and are ingested into engines from air and fuel sources, and impurities and oxidation products of engine components, such as iron oxide.

The term "operating temperature" means the surface temperature of the thermal barrier coating during its operation in a given application, such as a gas turbine engine. Such temperatures are above room temperature, and generally are above 500°C. High temperature operation of thermal barrier coated parts is usually above 1000°C.

DESCRIPTION OF THE INVENTION

It has been discovered that a composite comprising a thermal barrier coated part with at least two protective coatings on the ceramic thermal barrier coating exhibit decreased damage from environmental contaminants that form molten contaminant compositions at the operating temperatures of the engine system. The protective coatings are impermeable coatings, sacrificial oxide coatings, and non-wetting coatings.

Examples of composites of this invention include a thermal barrier coating and a bond coat on a part made of an alloy selected from the group consisting of nickel based alloys, cobalt based alloys, iron based alloys, and mixtures thereof, with the following protective layers: an impermeable

- 6 -

barrier first coating and a sacrificial oxide second coating; an impermeable barrier first coating with a non-wetting second coating; an impermeable barrier first coating with another type of an impermeable barrier as a second coating; an impermeable barrier first coating with a sacrificial oxide second coating and a non-wetting third coating: a sacrificial oxide first coating and an impermeable barrier second coating; a sacrificial oxide first coating and a non-wetting second coating; a sacrificial oxide first coating, an impermeable barrier second coating, and a non-wetting third coating. It is to be pointed out that the non-wetting coating is always the outer or last coating. Either the impermeable barrier coating or the sacrificial oxide coating may be the first coating on the thermal barrier coating.

The purpose of the multiple coatings is to protect the thermal barrier coating against damage from environmental contaminant compositions at operating temperatures. Sources of environmental contaminants include, but are not limited to, sand, dirt, volcanic ash, fly ash, cement, runway dust, substrate impurities, fuel and air sources, oxidation products from engine components, and the like. At operating temperatures of the thermal barrier coating, the environmental contaminants adhere to the surfaces of thermal barrier coated parts. The environmental contaminants then form contaminant compositions on surfaces of the thermal barrier coating which may have melting ranges or temperatures at or below the operating temperature.

In addition, the environmental contaminant may include magnesium, calcium, aluminum, silicon, chromium, iron, nickel, barium, titanium, alkali

SUBSTITUTE SHEET (RULE 26)

- 7 -

metals, and compounds thereof, to mention a few. The environmental contaminants may be oxides, phosphates, carbonates, salts, and mixtures thereof.

The chemical composition of the contaminant composition corresponds to the composition of the environmental contaminants from which it is formed. For example, at operational temperatures of about 1000°C or higher, the contaminant composition corresponds to compositions in the primary phase field of calcium-magnesium-aluminum-silicon oxide systems or CMAS. Generally, the environmental contaminant compositions known as CMAS comprise primarily a mixture of magnesium oxide (MgO), calcium oxide (CaO), aluminum oxide (Al₂O₃), and silicon oxide (SiO₂). Other elements, such as nickel, iron, titanium, and chromium, may be present in the CMAS in minor amounts when these elements or their compounds are present in the environmental contaminants. A minor amount is an amount less than about ten weight percent of the total amount of contaminant composition present.

The chemical composition of a CMAS eutectic mixture was determined by electron microprobe analysis of infiltrated deposits found on thermal barrier coated engine parts where deposit-induced damage to the thermal barrier coating had been observed. Analysis indicated that 127 microns (5 mils) of CMAS-like deposits (~34 mg/cm² assuming a density of 2.7 g/cm³) can form on thermal barrier coating surfaces. The CMAS deposits evaluated were typically in the compositional range (weight %): 5-35% CaO, 2-35% MgO, 5-15% Al₂O₃, 5-55% SiO₂, 0-5% NiO, 5-10% Fe₂O₃, however the content of the ubiquitous Fe₂O₃ can be as large as 75 wt%. An average composition for such deposits (weight %: 28.7% CaO, 6.4% MgO, 11.1% Al₂O₃,

SUBSTITUTE SHEET (RULE 26)

- 8 -

43.7% SiO₂, 1.9% NiO, 8.3% Fe₂O₃) was synthesized in the laboratory and used as a standard CMAS for the purpose of evaluating protective coatings.

Differential thermal analysis of actual CMAS deposits and the synthesized CMAS indicated that the onset of melting occurs at about 1190°C with the maximum of the melting peak occurring at about 1260°C. Thermal testing of candidate protective coatings for thermal barrier coatings versus the laboratory synthesized CMAS composition were carried out at about 1260°C.

Viscosity data on a similar CMAS composition indicates that the viscosity of CMAS is about 4 Pa·s (Pascal second) at 1260°C. This fluid phase infiltrates the TBC and induces TBC damage either by freezing-induced spallation or by high temperature chemical attack induced destabilization. Laboratory experiments with unprotected thermal barrier coatings indicate that, under isothermal conditions, 8mg CMAS/cm² is sufficient to cause entire thermal barrier coating layers to spall off.

To protect the thermal barrier coating from environmental contaminant compositions, such as CMAS, multiple protective coatings are used. Each protective coating is now discussed in turn, starting with impermeable barrier coatings, sacrificial oxide coatings, and then non-wetting coatings.

Impermeable barrier coatings are ceramic or metal layers. The coatings can be various oxides; non-oxides such as carbides, silicides, and nitrides; and metals that form non-porous deposits. The metal oxide coating is selected from the group consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide, calcium zirconate, and spinels, such as MgAl₂O₄,

- 9 -

mixtures thereof, and the like. The metal carbide coating is selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon oxy carbide (SiOC), mixtures thereof, and the like. The metal nitride coating is selected from the group consisting of silicon nitride, zirconium nitride, tantalum nitride, boron nitride, mixtures thereof, and the like. The metal silicide is selected from the group consisting of chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, mixtures thereof, and the like. Precious metals that are suitable for coatings include platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and alloys thereof, such as 80 weight percent palladium-20 weight percent silver.

Impermeable barrier coatings that are especially effective are a palladium-silver alloy, in particular about 80 weight % palladium-20 weight % silver, palladium, platinum, silicon carbide (SiC), silicon oxide (SiO₂), tantalum oxide (Ta₂O₅), calcium zirconate (CaZrO₃), spinel (MgAl₂O₄), silicon oxy carbide (SiOC), and mixtures thereof.

The impermeable barrier coating is deposited on thermal barrier coated parts by methods known in the art, such as sol-gel, sputtering, air plasma spray, organo-metallic chemical vapor deposition, physical vapor deposition, chemical vapor deposition, and the like. Thicknesses of the impermeable barrier coating can vary from about 0.2 micrometers to about 250 micrometers. About 2-125 micrometers is a preferred thickness for the impermeable barrier coating. Also, if thick impermeable barrier coatings are used (about 125

SUBSTITUTE SHEET (RULE 26)

- 10 -

micrometers or more), a graded deposit may be necessary to keep internal stresses minimized in order that coating delamination does not occur.

An effective amount of an impermeable
5 barrier coating is an amount needed to inhibit the contaminant composition from penetrating an opening in the thermal barrier coating. The thickness of the impermeable barrier coating is determined by the application and design of the thermal barrier coated
10 part, the amount and composition of the contaminant composition that is encountered during service, and the temperature that the thermal barrier coated part is operated at.

In this invention, the sacrificial or
15 reactive coating is usually a metal oxide, that reacts chemically with the contaminant composition at the surface temperature of the thermal barrier coating. The chemical reaction is one in which the sacrificial oxide coating is consumed, at least partially, and
20 elevates the melting temperature or viscosity of the contaminant composition. The melting temperature of the contaminant composition is preferably increased by at least about 10°C, and most preferably about 50-100°C, above the surface temperature of the thermal
25 barrier coating during its operation.

The composition of the sacrificial oxide coating is in part based on the composition of the environmental contaminants and the surface temperature of the thermal barrier coating during operation.
30 Usually, the sacrificial oxide coating contains an element or elements that are present in the liquid contaminant composition.

Suitable sacrificial oxide coatings that react with the CMAS composition to raise its melting

SUBSTITUTE SHEET (RULE 26)

- 11 -

temperature or viscosity, include, but are not limited to, alumina, magnesia, chromia, calcia, scandia, calcium zirconate, silica, spinels such as magnesium aluminum oxide, and mixtures thereof.

5 For instance, it has been found that a sacrificial oxide coating, such as scandia, can be effective in an amount of about 1 weight percent of the total CMAS composition present. Preferably, to
10 raise the CMAS melting temperature from 1190°C to greater than 1300°C, about 10-20 weight percent of scandia is used for the sacrificial oxide coating.

 As little as about one weight percent of the oxide coating based on the total weight of the
15 contaminant composition present on the surface of the coating can help prevent infiltration of molten
contaminant compositions into openings in the thermal barrier coating. Preferably, about 10-20 weight
20 percent of the sacrificial oxide coating is deposited on the impermeable barrier coating. In some
instances, the amount of the sacrificial oxide coating deposited may be up to fifty weight percent or a 1:1
ratio of oxide coating to liquid contaminant composition.

 The sacrificial oxide coating of the
25 composite is deposited on the thermal barrier coating or the impermeable barrier coating by methods known in the art, such as sol-gel, sputtering, air plasma
spray, organo-metallic chemical vapor deposition, physical vapor deposition, chemical vapor deposition,
30 and the like. Thicknesses of the sacrificial oxide coating can vary from about 0.2 micrometers to about 250 micrometers. The preferred thickness is about 2-125 micrometers. The thickness of the oxide coating is at least in part, determined by the chemistry of

SUBSTITUTE SHEET (RULE 26)

- 12 -

the particular oxide coating, the operating temperature of the thermal barrier coating, and the amount and composition of the contaminant. If thick sacrificial oxide coatings are required, i.e., about
5 125 micrometers or more, a compositionally graded deposit may be necessary to keep internal stresses minimized in order that delamination of the sacrificial coating does not occur.

In the practice of this invention, if the
10 surface temperature of the thermal barrier coating during operation is about 1200°C, then it is preferred to increase the melting temperature of the CMAS eutectic mixture to at least about 1210°C, and most preferably, to increase the CMAS melting temperature
15 to about 1260-1310°C, when using a sacrificial oxide coating. The melting temperature of the CMAS composition should be raised at least 10°C higher than the surface temperature of the thermal barrier coating during its operation.

20 Non-wetting protective coatings, deposited on the impermeable barrier coating or the sacrificial oxide coating, can be various oxides; non-oxides such as carbides, nitrides, and silicides; and precious metals. The oxide coating is selected from the group
25 consisting of silicon oxide, zirconium oxide, hafnium oxide, beryllium oxide, lanthanum oxide, and mixtures thereof. The carbide coating is selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, and mixtures
30 thereof. The nitride coating is selected from the group consisting of silicon nitride, aluminum nitride, titanium nitride, zirconium nitride, hafnium nitride, niobium nitride, tantalum nitride, boron nitride, and mixtures thereof. The silicide coating is selected

SUBSTITUTE SHEET (RULE 26)

- 13 -

from the group consisting of chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, and mixtures thereof. Metals that are suitable for coatings include platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and mixtures thereof.

Non-wetting coatings that are especially effective are a palladium-silver alloy, in particular about 80 weight % palladium-20 weight % silver, palladium, platinum, aluminum nitride (AlN), boron nitride (BN), silicon carbide (SiC), molybdenum silicide (MoSi₂), silicon oxide (SiO₂), zircon (ZrSiO₄), silicon oxy carbide (SiOC), and mixtures thereof.

The non-wetting coating is deposited on thermal barrier coated parts by methods known in the art, such as sol-gel, sputtering, air plasma spray, organo-metallic chemical vapor deposition, physical vapor deposition, chemical vapor deposition, and the like. Thicknesses of the non-wetting coating can vary from about 0.2 micrometers to about 250 micrometers. A preferred thickness of the non-wetting coating is about 2-125 micrometers. If thick non-wetting protective coatings are required (about 125 micrometers or more), a graded deposit may be necessary to keep internal stresses minimized in order that coating delamination does not occur.

An effective amount of a non-wetting coating is an amount needed to inhibit the environmental contaminants and contaminant eutectic mixture from adhering to the surface of a thermal barrier coated part. An effective amount of the non-wetting coating also decreases infiltration of the contaminant eutectic mixture into an opening of the

SUBSTITUTE SHEET (RULE 26)

- 14 -

thermal barrier coating. The thickness of the non-wetting coating is determined by the choice of coating, the application of the TBC part and its operational temperature, and the amount of the
5 contaminant eutectic mixture that is encountered.

Non-wetting coatings are selected based on the surface temperature of the TBC part during its operation and the composition of the environmental contaminants. The non-wetting protective coating must
10 have a melting temperature above the operational temperature of the thermal barrier coated part. For instance, if an operational temperature of a thermal barrier coated part is about 900°C, then the non-wetting protective coating has a melting temperature
15 above 900°C.

In accordance with this invention, the thermal barrier coating-protecting-composite is described in the following examples in terms of a impermeable barrier coating adjacent to the thermal
20 barrier coating. However, it is contemplated that the other protective coatings, i.e. sacrificial oxide coating, can be adjacent to the thermal barrier coating in combination with a secondary or even ternary protective coating.

EXAMPLES

25 Composites with sacrificial oxide coatings on thermal barrier coated parts were investigated to prevent the infiltration of environmentally deposited mixtures of oxides of calcium, magnesium, aluminum, and silicon (CMAS).

30 Survey studies of candidate coatings were conducted using differential thermal analysis (DTA) and thermodynamic calculation to assess the ability of candidate sacrificial materials to react with CMAS and

- 15 -

increase the melting temperature such that infiltration of the CMAS does not occur into the thermal barrier coating during service. Viscosity measurements were used to assess the ability of
5 sacrificial oxide coatings to react with CMAS, to increase the liquid phase viscosity, and thereby, to limit physical infiltration into the thermal barrier coating microstructure. Sessile drop contact angle
10 measurements were made to assess the non-wetting nature of the protective coating. Mercury porosimetry was used to assess the impermeable nature of the secondary coating.

Candidate composite coatings were deposited on thermal barrier coated substrates and assessed for
15 CMAS infiltration resistance. Coatings were deposited by screen printing, sol-gel, air plasma spray, sputtering, and MOCVD methods.

The effectiveness of protective coatings in preventing CMAS-infiltration-induced thermal barrier
20 coating damage was tested by comparing the infiltration resistance of protected and non-protected thermal barrier coated substrates which were thermally cycled in the presence of surface deposits of CMAS. In these experiments, 8mg/cm² of ground pre-reacted
25 CMAS was deposited on masked areas of the thermal barrier coated substrates. A thermal cycle consisted of heating the samples to 1260°C in 10 minutes, holding it at 1260°C for 10 minutes, followed by cooling it to room temperature in 30 minutes. After
30 each cycle the samples were inspected with the unaided eye and at 50x using a stereo microscope. This cycle was repeated several times. After completion of thermal testing, the samples were sectioned, metallographically polished, and inspected using

- 16 -

bright field and dark field optical microscopy, SEM and electron microprobe chemical analysis.

EXAMPLE 1

Example 1 demonstrates the effect of CMAS
5 on a thermal barrier coated part without a protective coating. Non-protected thermal barrier coating samples tested in the above-mentioned fashion exhibit visible CMAS induced thermal barrier coating swelling and cracking (visible on sample edge with
10 stereomicroscope). Metallographic preparation and inspection of the non-protected samples shows CMAS induced thermal barrier coating densification, cracking and exfoliation.

EXAMPLE 2

15 Example 2 demonstrates an impermeable barrier coating adjacent to the thermal barrier coating with a sacrificial coating. A thick film (125 micrometers) of 80 weight percent palladium-20 weight percent silver was deposited by thick film screen
20 printing of electrode paste on a 8 weight percent yttria-stabilized 92 weight percent zirconia coated coupon. The palladium-silver coating formed a dense, continuous film without voids. A scandia coating was deposited on the coated coupon. When about eight
25 mg/cm² CMAS are deposited on the top surface of the protected TBC, and thermally cycled, the underlying thermal barrier coating was not damaged as in Example 1.

EXAMPLE 3

30 Example 3 demonstrates two impermeable barrier coatings adjacent to the thermal barrier coating. A thick film (125 micrometers) of 80 weight percent palladium-20 weight percent silver was deposited by thick film screen printing of electrode

SUBSTITUTE SHEET (RULE 26)

- 17 -

paste on a 8 weight percent yttria-stabilized 92 weight percent zirconia coated coupon. The palladium-silver coating formed a dense, continuous film without voids. A spinel coating was then deposited to provide
5 a second impermeable barrier on the coated coupon. When about eight mg/cm² CMAS are deposited on the top surface of the protected TBC, and thermally cycled, the underlying thermal barrier coating was not damaged as in Example 1.

SUBSTITUTE SHEET (RULE 26)

- 18 -

What is claimed:

1. A protected thermal barrier coated composite comprising a thermal barrier coating on a part with a continuous first protective coating covering an outer surface of the thermal barrier coating and at least one second protective coating covering the first protective coating.
2. A composite according to claim 1 where the first protective coating is a sacrificial oxide coating or an impermeable barrier coating.
3. A composite according to claim 2 where the sacrificial oxide coating is selected from the group consisting of alumina, magnesia, chromia, calcia, calcium zirconate, scandia, silica, magnesium aluminum oxide, and mixtures thereof.
4. A composite according to claim 3 where an effective amount of the sacrificial oxide coating increases a melting temperature of a contaminant eutectic mixture about 10°C above a surface temperature of the thermal barrier coated part at operational temperatures.
5. A composite according to claim 2 where the impermeable barrier coating is selected from the group consisting of a metal oxide, a metal carbide, a metal nitride, a metal silicide, a precious metal, and mixtures thereof, where the metal oxide coating is selected from the group consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide, $MgAl_2O_4$, calcium zirconate, and mixtures thereof, where the metal carbide coating is selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon oxy carbide (SiOC), and mixtures thereof, where the metal nitride coating

SUBSTITUTE SHEET (RULE 26)

- 19 -

is selected from the group consisting of silicon
15 nitride, zirconium nitride, tantalum nitride, boron
nitride, and mixtures thereof, where the metal
silicide coating is selected from the group consisting
of chromium silicide, molybdenum silicide, tantalum
silicide, titanium silicide, tungsten silicide,
20 zirconium silicide, and mixtures thereof, and where
the precious metal coating is selected from the group
consisting of platinum, palladium, silver, gold,
ruthenium, rhodium, iridium, and mixtures thereof.

6. A composite according to claim 1 where
the second protective coating is an impermeable
barrier coating, a sacrificial oxide coating, or a
non-wetting coating, where the impermeable barrier
5 coating is selected from the group consisting of a
metal oxide, a metal carbide, a metal nitride, a metal
silicide, a precious metal, and mixtures thereof,
where the metal oxide coating is selected from the
group consisting of silicon oxide, tantalum oxide,
10 scandium oxide, aluminum oxide, hafnium oxide,
zirconium oxide, MgAl_2O_4 , calcium zirconate, and
mixtures thereof, where the metal carbide coating is
selected from the group consisting of silicon carbide,
tantalum carbide, titanium carbide, tungsten carbide,
15 silicon oxy carbide (SiOC), and mixtures thereof,
where the metal nitride coating is selected from the
group consisting of silicon nitride, zirconium
nitride, tantalum nitride, boron nitride, and mixtures
thereof, where the metal silicide coating is selected
20 from the group consisting of chromium silicide,
molybdenum silicide, tantalum silicide, titanium
silicide, tungsten silicide, zirconium silicide, and
mixtures thereof, and where the precious metal coating
is selected from the group consisting of platinum,
25 palladium, silver, gold, ruthenium, rhodium, iridium,

- 20 -

and mixtures thereof; the sacrificial oxide coating is selected from the group consisting of alumina, magnesia, chromia, calcia, calcium zirconate, scandia, silica, magnesium aluminum oxide, and mixtures thereof; and the non-wetting coating is selected from the group consisting of silicon oxide, zirconium oxide, hafnium oxide, beryllium oxide, lanthanum oxide, silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon nitride, aluminum nitride, titanium nitride, zirconium nitride, hafnium nitride, niobium nitride, tantalum nitride, boron nitride, chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and mixtures thereof.

7. A composite according to claim 1 where the protective coating is about 0.2-250 micrometers thick.

8. A composite according to claim 1 where the thermal barrier coating is a ceramic material.

9. A composite according to claim 8 where the ceramic material is a chemically stabilized zirconia selected from the group consisting of yttria-stabilized zirconia, scandia-stabilized zirconia, calcia-stabilized zirconia, magnesia-stabilized zirconia, and alumina-stabilized zirconia.

10. A composite according to claim 9 where the chemically stabilized zirconia is yttria-stabilized zirconia.

11. A composite according to claim 10 where the yttria-stabilized zirconia is about 8 weight percent yttria-92 weight percent zirconia.

12. A composite according to claim 1 where the part is an alloy selected from the group

- 21 -

consisting of nickel based alloys, cobalt based alloys, iron based alloys, and mixtures thereof.

13. A method for forming a thermal barrier coating-protecting-composite comprising: depositing an impermeable barrier or sacrificial oxide first coating on the thermal barrier coating, and then depositing at least one other protective second coating that is non-wetting, sacrificial or impermeable on the first coating.

14. A method according to claim 13 where a thickness of the protective first coating is about 0.2 micrometers to about 250 micrometers and the thickness of the protective second coating is about 0.2 micrometers to about 250 micrometers.

15. A method according to claim 13 where the protective first coating is deposited by sol-gel, sputtering, air plasma spray, organo-metallic chemical vapor deposition, physical vapor deposition, or chemical vapor deposition and the protective second coating is deposited by sol-gel, sputtering, air plasma spray, organo-metallic chemical vapor deposition, physical vapor deposition, or chemical vapor deposition.

16. A protected thermal barrier coated composite comprising at least two continuous protective coatings on an outer surface of a thermal barrier coating on a bond coat on a part.

17. A protected thermal barrier coated engine part comprising an engine structural component with a bond coat, a thermal barrier coating on the bond coat and at least two protective layers on the thermal barrier coating.

18. A composite according to claim 16 where the part is a turbine part.

SUBSTITUTE SHEET (RULE 26)

- 22 -

19. A composite according to claim 16 where the protective layers comprise a first protective coating selected from the group consisting of an impermeable barrier layer and a sacrificial layer, said layer being about 0.2 micrometers to about 250 micrometers thick, and a second protective coating selected from the group consisting of an impermeable barrier coating, a sacrificial oxide coating, and a non-wetting coating, said coating being about 0.2 micrometers to about 250 micrometers thick.

20. A composite according to claim 19 where the impermeable barrier coating is selected from the group consisting of a metal oxide, a metal carbide, a metal nitride, a metal silicide, a precious metal, and mixtures thereof, where the metal oxide coating is selected from the group consisting of silicon oxide, tantalum oxide, scandium oxide, aluminum oxide, hafnium oxide, zirconium oxide, $MgAl_2O_4$, calcium zirconate, and mixtures thereof, where the metal carbide coating is selected from the group consisting of silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon oxy carbide ($SiOC$), and mixtures thereof, where the metal nitride coating is selected from the group consisting of silicon nitride, zirconium nitride, tantalum nitride, boron nitride, and mixtures thereof, where the metal silicide coating is selected from the group consisting of chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, and mixtures thereof, and where the precious metal coating is selected from the group consisting of platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and mixtures thereof; the sacrificial oxide coating is selected from the group consisting of alumina, magnesia,

- 23 -

chromia, calcia, calcium zirconate, scandia, silica, magnesium aluminum oxide, and mixtures thereof; and the non-wetting coating is selected from the group consisting of silicon oxide, zirconium oxide, hafnium oxide, beryllium oxide, lanthanum oxide, silicon carbide, tantalum carbide, titanium carbide, tungsten carbide, silicon nitride, aluminum nitride, titanium nitride, zirconium nitride, hafnium nitride, niobium nitride, tantalum nitride, boron nitride, chromium silicide, molybdenum silicide, tantalum silicide, titanium silicide, tungsten silicide, zirconium silicide, platinum, palladium, silver, gold, ruthenium, rhodium, iridium, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/04461

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : B32B 9/00, 15/04; B05D 3/00, 3/12; B28B 17/00; F03B 3/12, 7/00

US CL : 428/469, 472, 701, 702; 427/331; 425/174; 416/241D

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/469, 472, 701, 702; 427/331; 425/174; 416/241D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
noneElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
none

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	US, A, 4,588,607 (MATRESE ET AL) 13 May 1986	1 10,12,16,19,20 ----- 11,13-15,17,18
X -- Y	US, A, 4,676,994 (DEMARAY) 30 June 1987, col.5, line 59	1-12,16,19,20 ----- 13-15,17,18

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understate the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

08 JUNE 1996

Date of mailing of the international search report

12 JUL 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

ARCHENE A. TURNER

Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/04461

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,080,977 (ZAPLATYNSKY) 14 January 1992, abstact	1-12,16,19,20
Y		13-15,17,18

Form PCT/ISA/210 (continuation of second sheet)(July 1992)*

THIS PAGE BLANK. (USP)